

Diffusion of Redox-Sensitive Elements in Basalt at Different Oxygen Fugacities. I. Szumila^{1,2}, D. Trail¹, L. R. Danielson² ¹University of Rochester (iszumila@gmail.com), Rochester, NY, ²Jacobs, JSC, 2224 Bay Area Blvd, Houston, Tx, 77058

Introduction: The terrestrial planets and moons of our solar system have differentiated over a range of oxygen fugacity conditions. Basalts formed from magmas on the Earth cover a range of more oxidized states (from \sim IW+2 to \sim FMQ+3) [1] than crustal rocks from Mars (IW to \sim IW+3), and basalts from the Moon are more reduced than both, ranging from IW to IW-2 [2]. The small body Vesta differentiated around IW-4 [3]. Characterization of redox sensitive elements' diffusivities will offer insight into behavior of these elements as a function of fO_2 for these planetary bodies.

Here, we report a systematic study of the diffusion of redox-sensitive elements in basaltic melts with varying oxygen fugacities (fO_2) for trace elements, V, Nb, W, Mo, La, Ce, Pr, Sm, Eu, Gd, Ta, and W. Since fO_2 is an intensive variable that is different for the reservoirs of various planets and moons in our solar system, it is important to characterize how changes in redox states will affect diffusion. We conducted experiments in a piston cylinder device at 1300 °C and 1 GPa, at the University of Rochester and NASA Johnson Space Center. We buffered some experiments at Ru-RuO₂ (FMQ+6.00), and conducted other experiments within either a graphite or Mo capsule, which corresponds to fO_2 s of either FMQ-1.2, or FMQ-3.00, respectively.

Characterizing the diffusivities of redox sensitive elements at different fO_2 s is important because some elements, like Eu, have varying valence states, such as Eu²⁺ and Eu³⁺. [4] Differences in charge and ion radii may lead to differences in diffusivities within silicate melts. This could lead to formation of a Eu anomaly by diffusion, the magnitude of which may be controlled by the fO_2 . Characterization of trace element diffusion is also important in understanding trace element fractionation. We found, during the course of our investigation, that not only did the diffusivities of the redox sensitive elements change with fO_2 , but that the diffusivities of all other analyzed elements also changed. This indicates that not only do changes in valence influence trace elements diffusivities but that the structure of melt may have changed with varying oxygen fugacity, probably due to changes in the speciation of the major element Fe.

Previous Work and Justification: Nakamura et al. (1998) [5] examined the diffusion of various trace elements in jadeite and diopside melts. These workers also discuss how polymerization of the melt affects diffusivity and how a Eu anomaly could be affected by the redox

state of the melt. Trail et al. (2012) [6] looked at the redox-sensitive elements Eu and Ce, and their anomalies in zircons as tracers of magmatic oxygen fugacity. Holycross and Watson (2016) [7] characterized diffusive fractionation of trace elements in basaltic melt using a graphite capsule to hold the sample charges. This research will help us understand the redox history of an element's source magma, and may be useful in understanding magma mixing.

Methods: A base mix of the major components of basalt and a trace mix of several elements including rare-earth elements were ground by hand in a mortar and pestle under ethanol. These were combined multiple times to make either a low trace element or high trace element glass. Trace elements were added in chondrite normalized proportions. Aliquots were fused in a platinum crucible using a 1-bar CO/CO₂ gas mixing furnace to 1300 °C for \sim 24 hours. This allowed for all glasses to be synthesized at an oxygen fugacity similar to the final piston cylinder run condition. After this, the synthesized glasses were ground into fine powders for \sim 20 minutes in acetone in preparation for piston cylinder diffusion experiments.

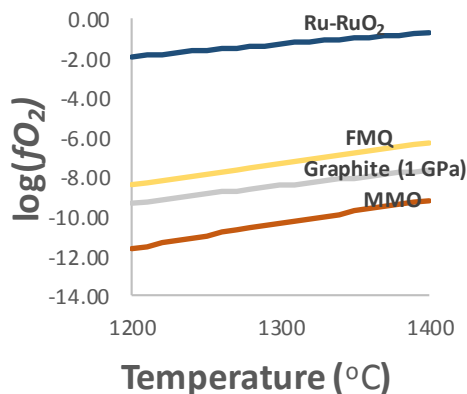


Figure 1. This figure shows the $\log(fO_2)$ buffers used in these experiments and the FMQ buffer for reference from 1200 °C to 1400 °C. The graphite buffer is notable since it has a strong dependence on pressure, which has been previously characterized [8].

Sample powders were packed with the high trace element material on the bottom and the low trace element material above it. Samples were pressurized and allowed to sit for at least one hour before heating. Experiments were heated to 1300 °C at 1 GPa in 7 minutes, and then allowed to dwell for 20, 40 and 80 minutes for each of the 3 oxygen fugacities explored. During quench,

pressure was kept constant at 1 GPa. Afterward, experiments were slowly depressurized to limit glass cracking.

Sample charges were sectioned lengthwise, mounted in epoxy and polished on sandpaper. Then polished with 1 μm alumina powder on an automatic polisher for approximately 30 minutes. Care was taken during the sample preparations phases to avoid cracking the glass phase and losing the sample.

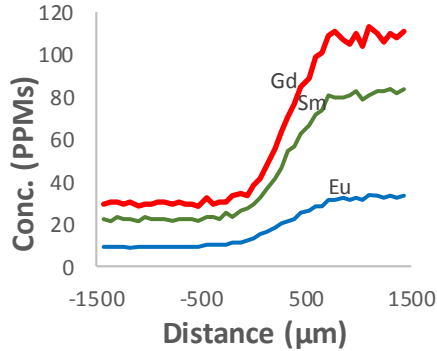


Figure 2. This figure plots the concentration of the elements Sm, Eu, and Gd from a 40 minute reducing case molybdenum capsule run. Green, blue and red are the concentration of Sm, Eu, and Gd respectively.

Analysis of diffusion couples was conducted via LA-ICP-MS on a 193 nm photon machines laser and an Agilent 7900 mass spectrometer. Spots were separated by 65 μm unless stated otherwise. Some samples were also mapped by LA-ICP-MS to see if samples showed any signs of convection rather than diffusive transport.

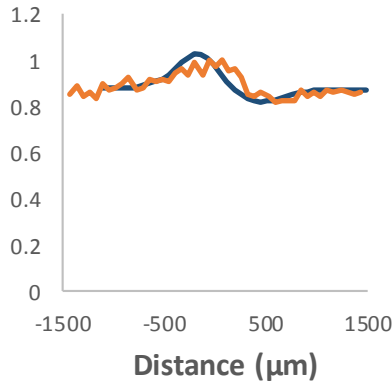


Figure 3. The blue line shows a simulation of the Europium anomaly using the diffusivities acquired from fitting the 40 minute molybdenum capsule run. The orange line is the experimental Europium ($\text{Eu}/\sqrt{\text{Sm} \cdot \text{Gd}}$) anomaly from the same run. Both lines have their highest point normalized to one.

Data from mass spectrometry was reduced using the Iolite software package. Elements that had a well-formed diffusion profile were selected to be used in a global fit. Iolite's global fit package was used for this purpose. Spots that fell on non-sample material or

cracks were masked out of the fit and the distance wave was adjusted to correct for this. The data were globally fit for each sample using equation 1.

$$C(x, t) = C_{+\infty} + \frac{C_{-\infty} - C_{+\infty}}{2} * (1 - \text{erf}(\frac{x - x_0}{2\sqrt{Dt}})) \text{ Eq. 1}$$

$C_{+\infty}$ and $C_{-\infty}$ are the concentrations of a particular element at positive and negative infinity. For any element whose diffusion has not yet reached the edge of the sample charge, this can be taken to be the concentration of the elements near the edge. It is also equivalent to the original concentration of the particular element in the starting high and low trace element powders if diffusion has not reached the edge of the sample. x_0 is the Matano interface, which can only have one value for all elements in the global fit on one sample charge. t was the time of the experiment in seconds and D was the diffusivity of a particular element in $\frac{\text{um}^2}{\text{s}}$. The variables that are allowed to vary in the global fit are $C_{+\infty}$, $C_{-\infty}$, D , and x_0 . $C(x, t)$ is the dependent variable, concentration along the diffusion couple which has been found via LA-ICP-MS. x is the position of each spot recorded by their distance apart from each other.

Results: Data have been obtained for experiments run using the Mo capsule and graphite capsule. Some further analysis is needed for the Ru-RuO₂ buffer case. There is no change in the acquired diffusivities as a function of time. However, diffusivities in the reducing conditions of a molybdenum capsule appear to be generally faster than those in more oxidizing conditions of a graphite capsule. This trend holds for not just the redox-sensitive elements but for all elements in the melt analyzed with the global fit.

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